

Ask Dr. ALOHA: Solutions and mixtures

In the “mystery scenario” described in the last issue, Rob, a firefighter in Hartford, Connecticut, had responded to an incident in which formaldehyde was released from a leaking container in an outbuilding at a university research laboratory (the

formaldehyde had leaked out onto an asphalt parking lot and formed an evaporating puddle). Later, he decided to model that spill in ALOHA. He remembered that at the time of the incident (early afternoon in late April), the wind speed was about 5 knots, under clear skies, and the temperature was about 50°F. He thought that the puddle was about 100 square feet in area, and perhaps half an inch deep, on average. He entered this information into ALOHA, and was very surprised by the results he obtained. Why was he surprised?

Running the release scenario

You can run this scenario in ALOHA to see what Rob found (first try some of the example problems in the ALOHA manual if you wish to review how to set up and run ALOHA scenarios). To do this:

- 1 Indicate the location of the release by choosing Hartford, Connecticut from the city library (choose **Location...** from the **SiteData** menu). Because you will not be estimating indoor formaldehyde concentrations, there’s no need to indicate building type.
- 2 Enter a date in late April, and an early afternoon time such as 14:00 (choose **Date & Time...** from the **SiteData** menu, then click **Set constant time**).
- 3 Choose formaldehyde from the chemical library (choose **Chemical...** from the **SetUp** menu).
- 4 Enter the weather conditions described above (choose **User Input...** from the **Atmospheric** submenu under the **SetUp** menu). Because Rob didn’t remember noticing any indications of a low-level atmospheric inversion, leave **No Inversion** selected. Because the release is in an urban area, choose “Urban or forest” to describe the ground roughness at the location. Leave the default relative humidity value of 50 percent unchanged, since you do not have a more accurate value.
- 5 Enter the puddle’s dimensions, as described above (choose **Puddle...** from the **Source** submenu under the **SetUp** menu). Since you don’t know the puddle and ground temperatures, set both equal to the air temperature.

ALOHA’s results

To Rob’s surprise, when he clicked **OK** on the second puddle data input screen, ALOHA displayed the following message:

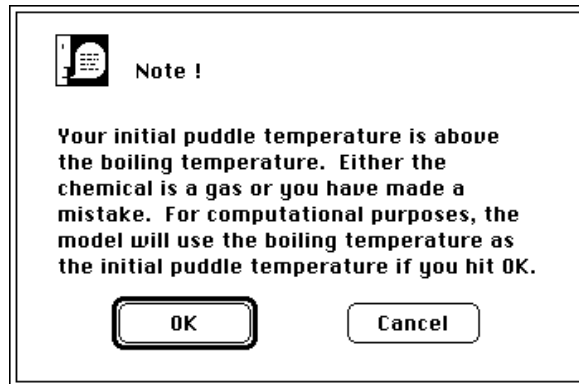


Figure 1. ALOHA displays this warning message if you attempt to use the Puddle source option to model a substance that is a gas at the given puddle temperature.

He checked the physical property information about formaldehyde displayed on the Text Summary screen, and found the statement:

Boiling Point: -2.38° F

This indicated to him that, contrary to his expectations, ALOHA expected the formaldehyde to be a gas under the conditions of his scenario, because the puddle temperature was higher than the boiling point of formaldehyde. In order to run the scenario that Rob had specified, ALOHA modeled the release as a “boiling puddle” case. It set the puddle’s temperature to the boiling point of pure formaldehyde (first alerting Rob before it did this), then predicted the rate of formaldehyde evaporation by assuming that the puddle would continue to boil either until it evaporated away or until an hour passed.

Text Summary	
SITE DATA INFORMATION:	
Location: HARTFORD, CONNECTICUT	
Building Air Exchanges Per Hour: 0.53 (Sheltered single storied)	
Date & Time: Fixed at April 30, 1995 & 1400 hours	
CHEMICAL INFORMATION:	
Chemical Name: FORMALDEHYDE	Molecular Weight: 30.03 kg/kmol
TLV-TWA: 0.30 ppm	IDLH: 30.00 ppm
Note: Potential or confirmed human carcinogen.	
Footprint Level of Concern: 30 ppm	
Boiling Point: -2.38° F	
Vapor Pressure at Ambient Temperature: greater than 1 atm	
Ambient Saturation Concentration: 1,000,000 ppm or 100.0%	
ATMOSPHERIC INFORMATION: (MANUAL INPUT OF DATA)	
Wind: 5 knots from w	No Inversion Height
Stability Class: B	Air Temperature: 50° F
Relative Humidity: 50%	Ground Roughness: Urban or forest
Cloud Cover: 1 tenths	
SOURCE STRENGTH INFORMATION:	
Puddle Area: 100 square feet	Average Puddle Depth: 0.5 inches
Soil Type: Concrete	Ground Temperature: 50° F
Initial Puddle Temperature: boiling point	
Release Duration: 48 minutes	
Max Computed Release Rate: 70.5 pounds/min	
Max Average Sustained Release Rate: 7.19 pounds/min	
(averaged over a minute or more)	
Total Amount Released: 212 pounds	

Figure 2. Rob's formaldehyde puddle evaporation scenario.

The explanation

ALOHA's treatment of this scenario did not square with Rob's experiences. He had responded to quite a few formaldehyde spills, and he had never encountered a boiling puddle of formaldehyde. Instead, he had observed that formaldehyde puddles do not boil, but instead evaporate slowly, much as a pool of water would do.

There is a simple explanation for the difference between ALOHA's results and Rob's experiences: ALOHA's chemical library contains information about *pure* formaldehyde. Pure formaldehyde is a gas at room temperature and atmospheric pressure. However, it's very unusual to encounter formaldehyde in its pure state. Instead, it is available commercially as a solution of formaldehyde in water. The boiling point of formaldehyde in solution depends on the percentage of formaldehyde present, but is much higher than typical ambient temperatures. For example, the boiling point of a 37 percent formaldehyde solution (by weight) is 207°F (97°C). Solutions containing common percentages of formaldehyde (about 37 to 50 percent formaldehyde by weight) therefore are liquid under most conditions.

Why isn't the solution in ALOHA's chemical library?

Rob wondered: since it is formaldehyde in solution that is commonly encountered, and pure formaldehyde is rare, why doesn't ALOHA's library contain formaldehyde solution rather than the pure chemical?

The answer has to do with the difficulty of modeling solutions and mixtures. When you first start up ALOHA, the model immediately presents you with a list of its limitations (Figure 3), which includes its inability to model mixtures and solutions. It is much harder to model a mixture or solution than to model pure chemicals because it's difficult to accurately predict properties such as vapor pressure for solutions or mixtures. For one thing, the properties of a solution like formaldehyde depend on the concentrations of the components of the solution (such as formaldehyde and water). Also, the properties of an evaporating solution change over time, because one component usually is more volatile (evaporates more readily) than the other component, so that its concentration within the solution drops over time. ALOHA's predictions of release rate and dispersion are greatly affected by vapor pressure and other properties. When an incorrect property value is used in ALOHA, the model's release rate and dispersion estimates will not be valid. For these reasons, *no solutions or mixtures are included in the chemical library.*

In fact, ALOHA users will soon discover that formaldehyde has been removed from ALOHA 5.2's chemical library. This was done because pure formaldehyde is so rare that emergency responders are very unlikely ever to encounter it, and to eliminate the risk of users unknowingly modeling the pure chemical when it is the solution which has been spilled.

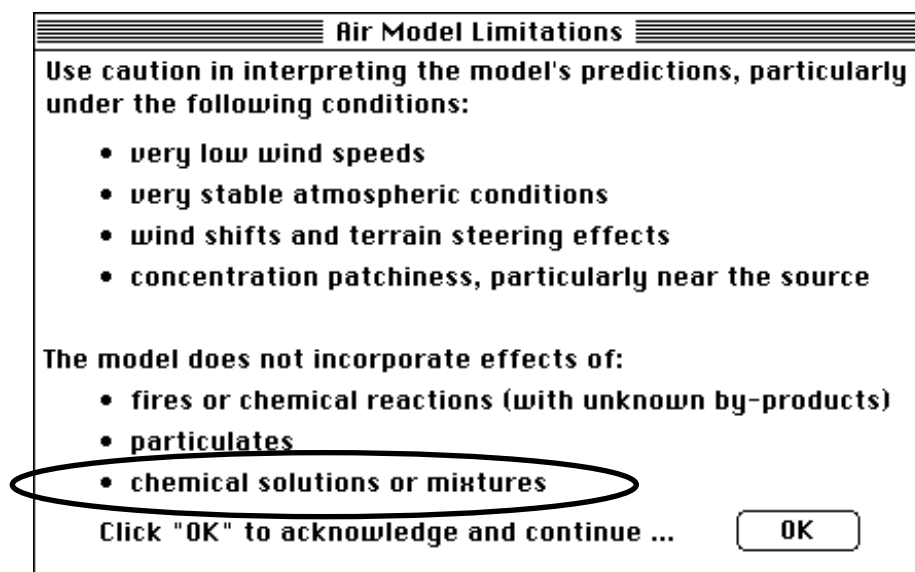


Figure 3. When you first start it up, ALOHA alerts you that it cannot model solutions or mixtures.

What can you do when you are responding to a spilled mixture or solution?

When you respond to a release of a chemical that you think may be in a mixture or solution rather than in pure form, bear in mind that it is the pure form, not the solution or mixture, that is included in ALOHA's library. Some ALOHA

chemicals are sometimes found in solution and sometimes found in pure form. Such chemicals include hydrogen chloride (a solution of hydrogen chloride in water is hydrochloric acid) and ammonia (generally called “anhydrous ammonia” when not diluted with water, and “ammonia solution” when in solution with water). Check to be sure that it is the pure form that has been spilled before modeling a release in ALOHA. Likewise, all acids, such as nitric acid and acetic acid, included in ALOHA’s library are assumed to be at nearly 100 percent concentration (rather than substantially diluted with water), but these acids often are stored, used, and transported in lower concentrations. If you’re responding to an acid spill, check to be sure that the acid is highly concentrated before modeling it in ALOHA.

Never try to model the evaporation and dispersion of a solution in ALOHA by modeling the pure chemical; you will not obtain accurate results. Instead, *recognize that ALOHA is not a useful tool for the incident.* Choose other tools, such as the Emergency Response Guidebook¹ (U. S. Department of Transportation 1993), which lists initial isolation and protective action distances for large and small spills of many hazardous substances. Knowing when ALOHA cannot help you is as important as recognizing when it can.

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¹ This guidebook (RSPA Publication P 5800.6) was developed by the Research and Special Programs Administration of the U. S. Department of Transportation, and is sold by the U.S. Government Printing Office, Superintendent of Documents, Mail Stop: SSOP, Washington, D.C. 20402-9328.